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(21) International Application Number: PCT/NL95/00161 (22) International Filing Date: 4 May 1995 (04.05.95) (30) Priority Data: 9400470 6 May 1994 (06.05.94) BE (71) Applicant (for all designated States except US): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): KAMER, Paulus, Clemens, Jozef [NL/NL]; Vroedschap 24, NL-1412 NW Naarden (NL). KRANENBURG, Mirko [NL/NL]; KNSM-Laan 620, NL-1019 LR Amsterdam (NL). VAN LEEUWEN, Petrus, Wilhelmus, Nicolaas, Maria [NL/NL]; Roerdomp 45, NL-3628 CA Kockengen (NL). DE VRIES, Johannes, Gerardus [NL/NL]; Bornedaal 33, NL-6228 GZ Maastricht (NL). (74) Agent: NIEUWKAMP, Johannes, Gerardus, Maria; Octrooi- bureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).	(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, IS, JP, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG). Published <i>With international search report.</i>	
(54) Title: BIDENTATE PHOSPHINE LIGAND (57) Abstract <p>The invention relates to a bidentate phosphine ligand, the phosphorous atoms of the phosphine being connected via a bridge group, the bridge group of the bidentate phosphine ligand consisting of an ortho-anellated annular system, comprising two aryl groups, which aryl groups are connected by two bridges, the first bridge consisting of an -O- or an -S- atom and the second bridge being a group that contains an oxygen, sulphur, nitrogen, silicon or carbon atom or a combination of these atoms, the two phosphorous atoms being connected to the two aryl groups of the bridge group at the ortho-position relative to the -O- or -S- atom of the first bridge. The invention also relates to the use of this bidentate phosphonium ligand in a catalyst system comprising also a transition metal compound which is used in the following type of reactions: hydroformylation, hydrogenation, hydrocyanation, polymerization, isomerisation, carboxylation, cross coupling and metathesis.</p>		

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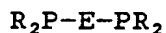
BIDENTATE PHOSPHINE LIGAND

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The invention relates to a bidentate phosphine ligand, the phosphorus atoms of the phosphine being connected via a bridge group.

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A bidentate phosphine ligand is a molecule having the following general structural formula:



(1)

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where E stands for a bridge group and R stands for the same or different organic groups, the bond between the organic bridge group and the phosphorus atom being a phosphorous-carbon bond.

Such a ligand is described in WO-A-87,07,600.

20 According to this publication such a ligand, for example 2,2'-bis(diphenylphosphinomethyl)-1,1'-biphenyl (BISBI), is particularly suitable for use in the hydroformylation of unsaturated organic compounds, catalysed with the aid of a transition metal compound based on rhodium. When use

25 is made of the BISBI ligand in combination with a rhodium compound, in the hydroformylation of 1-octene, we have found that the selectivity to normal C₉ aldehydes proves to lie around 70-75% and the molar normal/iso ratio of the C₉ aldehydes formed decreases from 15 to 4 at increasing

30 degree of conversion. The molar normal/iso ratio (n/iso ratio) is here and hereafter to be understood as the molar ratio of linear aldehydes and branched aldehydes.

A drawback of the state of the art is that a considerable amount of by-products is formed when using

35 the above mentioned ligands. The proportion of by-products (e.g. due to isomerisation), expressed as a percentage of the amount of converted 1-octene, is over 10%.

For many applications a high n/iso ratio is desired in addition to a high aldehyde selectivity.

The aim of the invention is to provide a ligand with which, in combination with a transition metal compound, the catalytic hydroformylation of unsaturated organic compounds is possible with a high selectivity towards aldehydes and thus less by-products are formed.

This aim is achieved in that to the bridge group of the bidentate phosphine ligand consists of an ortho-anellated annular system comprising two aryl groups, which aryl groups are connected by two bridges, a first bridge (bridge 1) consisting of an -O- or an -S- atom and a second bridge (bridge 2) being a group that contains an oxygen, sulphur, nitrogen, silicon or carbon atom or a combination of these atoms, the phosphorus atoms being connected to the two aryl groups of the bridge group at the ortho position relative to the -O- or -S- atom of the first bridge.

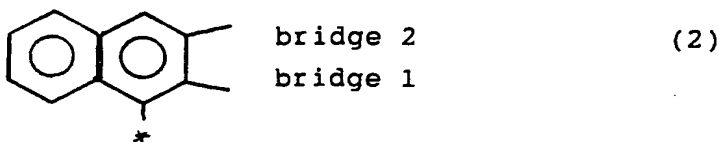
It has been found that when the ligand according to the invention is used in combination with a rhodium compound in the hydroformylation of unsaturated organic compounds, 50% less by-products are formed than when a ligand according to WO-A-8707600 is used. An additional advantage is that the n/iso ratio of the aldehydes formed is higher, especially when terminally unsaturated organic compounds are used as the starting material. A further advantage is that the ligands according to the invention are considerably more stable in air (or oxygen) than the ligands according to WO-A-8707600.

Another advantage of the ligand according to the invention is that it can not only be used as part of a catalyst system for a hydroformylation reaction but also as part of a catalyst system for other catalytic processes like e.g. hydrogenation, hydrocyanation, polymerisation, isomerisation, carbonylation, cross-coupling and metathese. The ligand according to the invention will generally form the catalyst system in combination with a catalytically active metal. It has been found that the ligand according to the invention is particularly suitable

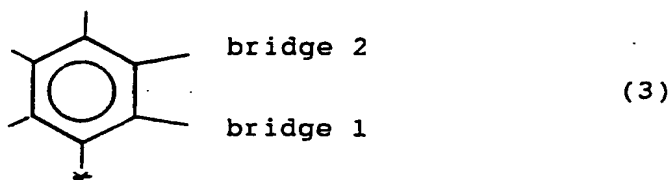
for use as catalyst system in the hydroformylation of unsaturated organic compounds in combination with a transition metal compound, the metal of which is for example rhodium, ruthenium, cobalt, palladium or platinum.

- 5 Of the transition metals mentioned, rhodium is a particularly preferred metal.

The aryl groups in the bridge group generally contain between 6 and 14 carbon atoms and may each individually consist of a single-ring structure, whether
10 or not substituted, or of an anellated structure of 2 or more condensed rings, like



Preferably, the aryl groups have the following structure

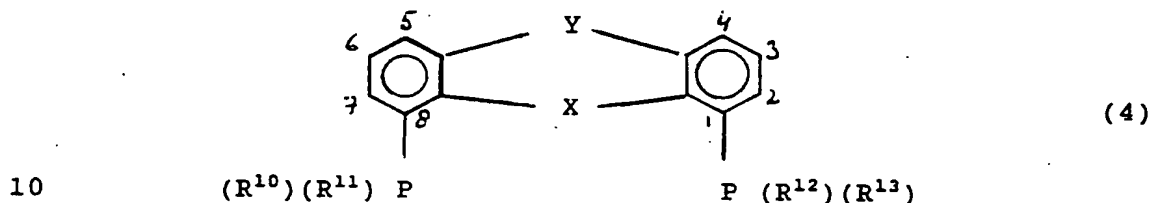


where the phosphorus atom of the phosphine is bound to the aryl group at the ortho-position relative to the first bridge (* in formula 2 and 3) and the aryl group(s) may or
25 may not be substituted.

The second bridge in the bidentate phosphine ligand generally contains an -O-, -S-, -N(R¹)-, -N⁺(R²)(R³)-, -Si(R⁴)(R⁵)-, -P(O)(R⁶)-, -C(R⁷)(R⁸)- group, or a combination of a -C(R⁷)(R⁸)-group with one of the
30 groups mentioned, R¹ being a hydrogen atom or an organic group having between 1 and 20 carbon atoms or a polymer, R² and R³ being organic groups, which may or may not be the same, having between 1 and 20 carbon atoms or a polymer, R⁴ and R⁵ being organic groups, which may or may not be the
35 same, having between 1 and 10 carbon atoms, R⁶ being a hydroxide group or an organic group having between 1 and 10 carbon atoms and R⁷ and R⁸ being organic groups, which

may or may not be the same, having between 1 and 10 carbon atoms.

The bidentate phosphine ligand according to the invention may for example have a structure according to
5 formula (4):



where X stands for the first bridge and Y for the second bridge, and where R^{10} , R^{11} , R^{12} and R^{13} stand for organic groups, which may or may not be the same, having between 1
15 and 14 carbon atoms.

X is preferably an -O- atom. Y is preferably not an -O- atom if X stands for an -O- atom because such ligands are easier to prepare.

R^1 in the $-N(R^1)-$ group may be a hydrogen atom or
20 an organic group having between 1 and 20 carbon atoms or a polymer. If R^1 is an organic group, R^1 is preferably an aralkyl group, for example benzyl, or an alkyl group, for example a methyl, ethyl, propyl, isopropyl, n-butyl or isobutyl group. R^1 may also be an alkylidene group having
25 between 2 and 20 carbon atoms, with which the ligand can be connected to a solid carrier for example silica or a polymer, for example polyethylene. R^1 may be a polymer that serves as a carrier.

R^2 and R^3 in the $-N^+(R^2)(R^3)-$ group are organic
30 groups, which may or may not be the same, having between 1 and 20 carbon atoms. Examples of possible groups are aralkyl groups, for example benzyl, and alkyl groups, for example a methyl, ethyl, propyl, isopropyl, n-butyl or isobutyl group. R^2 and/or R^3 may also be an alkylidene
35 group having between 2 and 20 carbon atoms, with which the ligand can be connected to a solid carrier for example silica or a polymer, for example polystyrene. R^2 and/or R^3

may also be a polymer that serves as a carrier.

The $-N^+(R^2)(R^3)-$ group may be used with advantage because a bidentate phosphine ligand comprising such a bridge 2 is better soluble in water. This is of use in processes in which the catalyst system is separated using an aqueous medium from an organic reaction mixture. In general, the choice of the anionic counter ion is not critical. If the bidentate phosphine ligand is used in a catalyst, for example in the hydroformylation, use is generally made of an anionic counter ion that do not adversely affect the reaction. Examples of anionic counter ions are $R^{16}-SO_3^-$, $R^{16}-CO_2^-$ and $R^{16}-PO_3^{2-}$, where R^{16} stands for hydrogen or an alkyl group having between 1 and 12 carbon atoms or an aralkyl, alkaryl or aryl group having between 6 and 12 carbon atoms, for example a methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, phenyl or benzyl group.

R^4 and R^5 in the $-Si(R^4)(R^5)-$ group are organic groups, which may or may not be the same, having between 1 and 10 carbon atoms. Examples of possible organic groups are alkyl, aralkyl, alkaryl and aryl groups. Examples of such groups are methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, phenyl and benzyl groups. R^4 and R^5 can together form a ring having between 2 and 6 carbon atoms.

R^6 in the $-P(O)(R^6)-$ group is a hydroxide group or an organic group having between 1 and 10 carbon atoms, for example an aryl, alkyl, aryloxy or alkoxy group. Examples of these groups are the phenyl, benzyl, methyl, ethyl, naphthyl, phenoxy, cyclohexyloxy and 2-tert-butylphenoxy groups.

R^7 and R^8 in the $-C(R^7)(R^8)-$ group independently of one another stand for organic groups having between 1 and 10 carbon atoms. Examples of possible organic groups are the methyl, ethyl, propyl, isopropyl, butyl, isobutyl and the phenyl groups. R^7 and R^8 may together form a ring having between 2 and 6 carbon atoms.

R^{10} , R^{11} , R^{12} and R^{13} may independently of one

another be an alkyl, aryl, aralkyl, alkaryl or a cycloaliphatic group having between 1 and 14 carbon atoms, which may or may not be substituted. Preferably these groups are cycloalkyl or aryl groups having between 5 (or
5 6 in the case of aryl groups) and 14 carbon atoms. Most preferably these groups are phenyl, naphthyl, diphenyl or cyclohexyl groups.

The aryl groups in the bridge group and the aryl, aralkyl, alkaryl or cycloalkyl groups R^{10} , R^{11} , R^{12}
10 and R^{13} may be substituted with organic groups containing between 1 and 10 carbon atoms, or with other groups, for example halogen groups or groups that increase the bidentate phosphine ligand's solubility in water. Possible organic groups are alkyl groups, for example the methyl,
15 ethyl, propyl, isopropyl, butyl, isobutyl and pentyl groups; alkoxy groups, for example the methoxy and ethoxy groups; cycloaliphatic groups, for example cyclopentyl, cyclohexyl; alkanoyl, for example acetyl, benzoyl; halogen groups, for example fluorine and chlorine; halogenated
20 alkyl groups, for example $-CF_3$; and ester groups, for example acetic esters. When R^{10} , R^{11} , R^{12} or R^{13} is a phenyl group, then alkoxy groups, alkyl groups, halogens and halogenated alkyl groups may with advantage be ortho- and para-substituted to the phenyl group.

25 Examples of substituents that increase the bidentate phosphine ligand's solubility in water are the carboxylate group, $-COOM$, the sulphonate group, the $-SO_3M$, phosphate group, the $-PO_3M_2$ and the ammonium salt $-N(R^{14})_3A$.

30 Suitable cations M are inorganic cations of metals, in particular of alkali and alkaline earth metals for example sodium, potassium, calcium or barium, and also ammonium ions or quaternary ammonium ions, for example tetramethyl ammonium, tetrapropyl ammonium or tetrabutyl
35 ammonium.

Suitable anions A are sulphate and phosphate groups and organic acid groups for example $R^{15}-SO_3^-$, $R^{15}-$

CO_2^- and $\text{R}^{15}\text{-PO}_3^{2-}$, where R^{15} may be an organic group having between 1 and 18 carbon atoms. Examples of suitable organic groups are alkyl, aralkyl, alkaryl and aryl groups.

5 Suitable R^{14} and R^{15} groups are aliphatic hydrocarbon groups having between 1 and 18 carbon atoms, for example the methyl, ethyl, n-butyl, isobutyl and pentyl groups.

 Examples of bidentate phosphine ligands
10 according to the invention are ligands 1 up to and including 31 represented on the formula sheet, Ph representing a phenyl group, a dash a methyl group and -Et an ethyl group.

 The invention also relates to a method for the
15 preparation of a bidentate phosphine ligand according to the invention. The ligand according to the invention can be prepared using methods that are, in itself, available to a person skilled in the art. The bidentate phosphine ligand can be prepared in a manner similar to that
20 described by M.W. Haenel, et al., Chem. Ber. 125 (1991) 1705-1710. In such a preparation of the ligand an organic compound, which corresponds to the bridge group of the ligand (having hydrogen atoms at the position at which the bonds to the phosphorus atoms will ultimately be), is
25 dissolved in a mixture of a suitable solvent, together with a strong base and an additional complexing agent, after which 2 or more equivalents of an organic phosphorous compound, optionally dissolved in a solvent, are added to the mixture, in which process the bidentate
30 phosphine ligand is formed. The ligand according to the invention can for example with advantage be prepared by dissolving a compound which is the same as the bridge group of the ultimate ligand (i.e. without the phosphorus atoms), in a suitable solvent. Suitable solvents are for
35 example ether, for example diethyl ether, tetrahydrofuran or dioxane, or an aliphatic hydrocarbon, for example hexane or cyclohexane, or a mixture of these solvents.

Subsequently a strong base is added to this solution, for example n-BuLi (BuLi= butyl lithium), s-BuLi or t-BuLi. Other strong bases based on K, Na and Mg are also suitable for this purpose. The strong base is generally added at a low temperature, for example of between -80 and 0°C, after which the temperature of the mixture is slowly increased to for example room temperature. It is advantageous to add an extra complexing agent for the strong base, for example tetramethylethylene diamine or tetramethylurea. This complexing agent for the strong base may be added before or after the addition of the base. The mixture thus obtained is mixed for a certain period of time (generally between 10 and 20 hours) at a temperature that is generally between -80 and 80°C, in the process of which a 1,8-bis-metallised compound is formed. Then the solution is again cooled to a temperature of between -80 and 0°C. A mixture containing 2 or more equivalents of Ar₂PZ (Ar corresponding to the ultimate R¹⁰, R¹¹, R¹² and R¹³ groups, Z standing for a halogen atom or an alkoxy group having between 1 and 4 carbon atoms; suitable halogen atoms being Cl, Br and I) and optionally a solvent, for example hexane or tetrahydrofuran, is then added. After some time, for example 10-20 hours' stirring at for example room temperature, the reaction mixture is further extracted with an aqueous solution and dried. The product may be for example purified through crystallisation.

The invention also relates to a catalyst system comprising a bidentate phosphine ligand and a transition metal compound in which the bidentate phosphine ligand is a ligand according to the invention.

The bidentate phosphine ligand/transition metal compound ratio is generally between 0.5 and 100. Preferably this ratio is between 0.5 and 10. The ratio chosen proves to have little effect on the selectivity towards aldehydes, but for practical reasons, for example the solubility of the ligand and the transition metal compound cost price, it will usually lie within the

aforementioned limits.

For hydroformylation reactions the transition metal compound is preferably based on a rhodium compound. Such a catalyst system can be prepared by dissolving the bidentate phosphine ligand and a rhodium compound in a solvent or in the reaction mixture. Examples of rhodium compounds that can be used are $\text{Rh}(\text{CO})_2(\text{t-C}_4\text{H}_9\text{-COCHCO-t-C}_4\text{H}_9)$, $\text{Rh}(\text{CO})_2(\text{acac})$ (acac=acetylacetonate), Rh_2O_3 , $\text{Rh}_4(\text{CO})_{12}$, $\text{Rh}_6(\text{CO})_{16}$, $[\text{Rh}(\text{OAc})_2]_2$ (OAc= acid residue of acetic acid) and rhodium (ethylhexanoate)₂. Preferably, $\text{Rh}(\text{CO})_2(\text{acac})$ or $[\text{Rh}(\text{OAc})_2]_2$ is used as the rhodium compound because these compounds can be easily obtained.

The invention also relates to a method for the preparation of an aldehyde through hydroformylation, using an ethylenically unsaturated organic compound as a starting material, in the presence of carbon monoxide, hydrogen and a catalyst system according to the invention. Preferably the transition metal compound is a rhodium compound.

Unsaturated compounds that can be hydroformylated to aldehydes using the method according to the invention are for example linear and branched unsaturated organic compounds having between 2 and 20 carbon atoms. The organic compounds may optionally contain functional groups. Examples of such functionalized unsaturated organic compounds are unsaturated carboxylic acids, esters, amides, acrylamides, nitriles, aldehydes, ketones, alcohols and ethers.

The organic compounds may be for example alkenes, for example ethylene, propylene, 1-butylene, 2-methylpropylene, 2-methyl-1-butylene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 2-ethyl-1-hexene, 1-dodecene, 1-octadecene, 1,5-hexadiene, 1,7-octadiene, 1,9-decadiene, 1,3-butadiene, isoprene, 1,3-pentadiene, 1,4-pentadiene, vinyl cyclohexene; aromatic compounds with one or more aliphatic unsaturated substituents, for example styrene; unsaturated esters, for example vinyl

acetate, alkyl acetate, alkyl propionate; alkyl acrylates, for example methyl methacrylate, methyl acrylat , ethyl acrylate; unsaturated aldehydes for example acroleïne, unsaturated carboxylic acids, for example 3-pentenoic acid
5 and 4-pentenoic acid; pentenoates, for example methyl-4-pentenoate, methyl-3-pentenoate; unsaturated ethers, for example allyl ethers, for example allyl ethylether; vinyl ethers, for example vinyl methylether, allyl ethylether; styryl ethers, for example styryl methylether or styryl
10 silylether; unsaturated acetals, for example the acetal of 4-pentenal and ethylene glycol; alkenols, for example allyl alcohol and 2,7-octadienol; unsaturated nitriles, for example 3- and 4-pentene nitrile; unsaturated amides, for example 5-hexene amide and alkyl acrylamides;
15 unsaturated silanes, for example vinyl silane; unsaturated siloxanes, for example vinyl siloxane.

The method according to the invention can also be used to convert unsaturated polymers into polymers with aldehyde groups. An example of such an unsaturated polymer
20 is 1,2-polybutadiene.

The method according to the invention is suitable for the preparation of aldehydes in which a high selectivity towards the total of aldehydes is obtained. If it is not important which aldehyde functionality is
25 ultimately formed (normal or iso), this method can with advantage be used for all the substrates mentioned above. If it is important that the aldehyde functionality is with a very high selectivity to be at the end of a carbon chain (i.e. high n/i ratio), use is preferably made of
30 terminally unsaturated organic compounds (the unsaturation being at the end of the molecule's carbon chain), a number of which have been mentioned as examples above. It has also been found that the reaction rate is highest when use is made of these terminally unsaturated organic compounds.

35 The reaction conditions under which the hydroformylation according to the invention can be carried out will be described below.

The temperature may be between 30 and 150°C. More preferably, the temperature is between 50 and 120°C. The pressure may be between 0.1 and 60 MPa. More preferably, the pressure is between 0.3 and 30 MPa, most preferably between 0.5 and 6 MPa.

The molar ratio of the hydrogen to carbon monoxide, added to the reaction zone or present during the reaction, may depend on the substrate and the chosen reaction conditions in a commonly known manner. The hydrogen/carbon monoxide molar ratio is generally between 0.5 and 4.0 during the hydroformylation. In some cases, however, the yield of desired product and also the reaction rate can be increased by choosing a ratio higher than 4.0. During the hydroformylation the total molar amount of carbon monoxide and hydrogen is generally 0.01 to 20 times the molar amount of unsaturated organic compound (substrate). More preferably this ratio is between 1.2 and 6.

The hydroformylation is generally carried out in the presence of a solvent. If so desired, the hydroformylation may however also be carried out without a solvent.

Organic solvents that are inert or do not interfere with the hydroformylation are suitable solvents. Examples of suitable solvents are the starting compound and the reaction product and compounds related to the product to be formed, for example by-products and in particular condensation products. Other suitable solvents are saturated hydrocarbons for example naphthas, kerosine, mineral oil and cyclohexane, and aromatic hydrocarbons, ethers, ketones, nitriles, amides and urea derivatives, for example toluene, benzene, xylene, Texanol[®] (Union Carbide), diphenylether, tetrahydrofuran, cyclohexanone, benzonitrile, N-methylpyrrolidone and N',N'-dimethylethylurea. The solvent and substrate are preferably free of catalyst poisons known for the hydroformylation, for example acetylene, butadiene, 1,2-propadiene, thiophenol,

dialkyldisulphide or HCl.

If a rhodium compound is used as transition metal compound in the catalyst system, the amount of rhodium in the reaction mixture may vary from $1 \cdot 10^{-6}$ to 0.1 mol of rhodium per mol of substrate. Low rhodium concentrations are however not attractive from a commercial point of view because then the reaction rate is not high enough. The upper limit is determined by rhodium's high raw material price. In principle there is no objection to choosing a rhodium concentration of above 0.1 mol per mol of substrate. However, this concentration is generally between $1 \cdot 10^{-5}$ and $5 \cdot 10^{-2}$ mol of Rh per mol of substrate. Preferably this concentration is between $1 \cdot 10^{-4}$ and $1 \cdot 10^{-2}$ mol of Rh per mol of substrate.

The residence times can vary considerably and depends on the desired degree of conversion, yield and/or selectivity of the reaction.

The hydroformylation may be carried out both batchwise as well as in continuous mode. The hydroformylation is generally carried out in continuous mode. The hydroformylation can for example be carried out in a so-called bubble reactor, liquid-overflow reactor, continuously stirred tank reactor or a trickle bed.

The invention also relates to a process for the preparation of esters by carbonylation of an unsaturated compound in the liquid phase in the presence of an alkanol, carbon monoxide, a bidentate ligand of the invention and a transition metal compound.

The unsaturated compound may be of the type described previously as substrate for hydroformylation reactions.

The alkanol as a rule has 1-20 carbon atoms. The alkanol may be an aliphatic, cycloaliphatic or aromatic compound. Examples of suitable alkanols are methanol, ethanol, propanol, cyclohexanol, phenol. The quantity of alkanol applied is not critical. Preferably, the molar ratio of alkanol:unsaturated compound is 1:1.

The metal in the transition metal compound used can be rhodium, ruthenium, palladium, platinum or cobalt; palladium is a preferred metal and a palladium based catalyst and its uses will be described below.

5 The actual catalyst system is a complex between the transition metal compound and the ligand. In these complexes other ligands next to the ligand according to the invention are used, for example halogen atoms; hydride; carboxylates; CO; solvents, for example acetonitrile, ether and the like; nitrogen bases, like pyridine, quinoline and dimethylaniline; olefins for example ethylene; or dienes for example cyclooctadiene; aryl groups bound through all or part of their π -orbitals for example η -6 benzene, or η -6 cumene.

15 Another way to create an active catalyst is by using a catalyst precursor, for example PdCl_2 , $\text{Pd}(\text{OAc})_2$, palladium nitrate, palladium on carbon in conjunction with 1 to 5 equivalents of the ligand of the invention. A more preferred ratio is between 1 and 2.

20 The ratio of catalyst to substrate can vary in between 10^{-1} and 10^{-6} , but more preferably lies between 10^{-2} and 10^{-4} .

It may also be advantageous to use a cocatalyst for example SnCl_2 , in a ratio of 1-5 equivalents with respect to the transition metal, to enhance the reactivity of the catalyst. If palladium is used as the transition metal the carbonylation is preferably carried out in the presence of a catalytic quantity of a protonic acid. The pK_a of the acid is dependant upon the type of unsaturated substrate. For conjugated substrates like 1,3-butadiene a protonic acid with $\text{pK}_a > 3$ (measured in water at 18°C) is used. Examples are benzoic acids preferably trimethylbenzoic acid and valeric acid. With non conjugated alkenes as substrates an acid with $\text{pK}_a < 3$ (measured in water at 18°C) like a sulfonic acid is used.

35 All inert solvents are in principle suitable as additional solvent, but it is also possible to use an

excess amount of one of the reactants, products or side products in such an amount that a suitable liquid phase is obtained. Examples of suitable solvents are sulfolane, toluene, esters, diphenyl ether and the like. If 1,3-butadiene is used as the unsaturated substrate, methyl valerate or pentenoate esters can be used advantageously as solvent.

The carbonylation is preferably carried out at CO pressures between 2 and 30 MPa, and more preferably between 5 and 20 MPa; the temperatures can range between 20 and 200°C, but more preferred are temperatures between 50 and 150°C.

The products of the above described carbonylation reaction are esters. If butadiene is used as a substrate a mixture of pentenoic esters, containing mostly 3-pentenoic ester, will be obtained. However, it is also possible by tuning of the reaction conditions like temperature and CO pressure to carbonylate 3-pentenoic ester or a mixture of pentenoic esters to obtain a mixture of diesters in which adipic ester is found the most abundantly. In a similar way it is possible to carbonylate 3-penteno-1-nitrile to obtain a mixture of nitrile esters in which 5-cyanopentanoic ester is the main product. Also, 3-pentenoic acid may be carbonylated to give a mixture of acid esters in which the adipic mono ester is the main product.

If in the carbonylation reaction described above, using the palladium based catalyst, the alkanol is replaced by water the product will be a carboxylic acid. In this case butadiene will give a mixture of pentenoic acids, containing mostly 3-pentenoic acid. Carbonylation of 3-pentenoic acid or mixtures of pentenoic acids will give rise to a mixture of di-acids containing mostly adipic acid.

If in the carbonylation reaction described above, using the palladium based catalyst, the alkanol is replaced by an amine, the product will be an amide.

If in the carbonylation reaction described above, using the palladium based catalyst, the alkanol is replaced by a thiol, the product will be a thioester.

The invention also relates to a process for
5 transition metal catalyzed hydrocyanation reactions of
olefins, polyenes and acetylenes to give nitriles. Whereas
the state of the art of transition metal catalyzed
hydrocyanation clearly prefers phosphite ligands or
ligands containing at least one POR bond (where R is an
10 aryl or alkyl group) for the hydrocyanation of olefins,
and whereas only highly reactive (strained) olefins like
norbornene and norbornadiene can be hydrocyanated in good
yield using conventional bisphosphine ligands, the ligands
of the invention can be used for the hydrocyanation of all
15 olefins for example 1-octene and styrene. Whereas
phosphite ligands are easily hydrolysed by water the
ligands of the invention are stable both in storage as
well as during the use in the hydrocyanation reaction.

The conventional hydrocyanation catalysts, based
20 on nickel in its zerovalent state in conjunction with
phosphite ligands, suffers from oxidation by hydrogen
cyanide (HCN), leading to the irreversible formation of
Ni(CN)₂ complexes which are catalytically inactive. This
can be countered by performing the hydrocyanation reaction
25 with low concentrations of HCN, but this has an adverse
effect on the productivity of the reaction. The ligands of
the invention form active catalysts with Nickel(0) that
show a remarkable resistance against oxidation by HCN and
remain active till the end of the reaction. This allows
30 the use of high concentrations of HCN leading to higher
productivity per unit of space and unit of time.

Several transition metals can serve to form
active hydrocyanation catalysts with the ligands of the
invention, for example Ni(0), Pd(0), Pt(0), Co(0) or
35 Co(I), Fe(0), Rh(I), Ru(II), Ir(I), Mo(0) or W(0). Of
these Ni(0) is the most preferred metal. Several methods
are available to form complexes of these metals with the

ligands of the invention. These complexes can be used as catalyst. However, it is also possible to use a catalyst precursor for example $\text{Ni}(\text{COD})_2$ (COD=cyclooctadiene) or $\text{Pd}(\text{DBA})_2$ (DBA=dibenzylideneacetone), in combination with
5 the ligands of the invention.

The ratio between ligand and metal may vary, the optimal ratio being different for each metal, but will usually lie between 1 and 5 and more preferred between 1 and 2. The catalyst can be used in ratios with respect to
10 the amount of substrate varying in between 10^{-1} and 10^{-6} mol%, but more preferred in between $5 \cdot 10^{-2}$ and 10^{-4} mol%.

A Lewis acid co-catalyst may be used in combination with the catalysts described above, but the hydrocyanation reaction can also be performed in the
15 absence of these co-catalysts. Many Lewis acids are suitable, for instance ZnCl_2 , AlCl_3 , Ph_3B or AlEtCl_2 .

The olefinic substrates used in the hydrocyanation may be terminal olefins, for example ethylene, propylene or 1-butene, but also internal
20 olefins, for example 2-octene; also a mixture of olefins may be hydrocyanated, to give terminal nitriles preferentially. The olefins may carry a variety of substituents: 3-pentenitrile or mixtures of isomeric pentenenitrile may be hydrocyanated to give dicyanobutane-
25 s, containing mostly adiponitrile. 3-pentenoic acids and their esters or isomeric mixtures thereof can be hydrocyanated to give cyanopentanoic acids or the esters, respectively. The linear products are predominant in the product mixtures.

30 Cyclic olefins like cyclohexene may also be hydrocyanated. Aromatic olefins, for example styrene may be hydrocyanated with these catalysts giving nitriles with extremely high iso to normal ratios.

Dienes or polyenes are also excellent substrates
35 for the hydrocyanation reaction. For instance butadiene may be hydrocyanated to give a mixture of pentenenitrile containing mostly 3-pentenitrile.

Acetylenic substrates like acetylene, propyne or 1-hexyne may be hydrocyanated with the catalysts of the invention to give olefinically unsaturated nitriles.

The HCN may be administered to the reaction mixture in liquid form, as a solution in an organic solvent, for example toluene, or as a gas sparged through the solution, or blown over the surface of the solution of the catalyst and the substrate.

Solvents that can be used are toluene, ethyl acetate, methyl tert-butyl ether, acetonitrile, sulfolane, diphenyl ether and the like, but the reaction can also conveniently be carried out without a solvent or with the substrate, the product or side products as solvent.

The reaction may be carried out at temperatures between -40°C and 120°C , but more conveniently between 0°C and 100°C .

There are many ways in which these hydrocyanation reactions can be conveniently carried out. These have been described in detail in the abundantly available literature. A number of examples are presented in the experimental section.

The ligands of the invention can also be used in combination with transition metals for the hydrogenation of olefins, dienes, alkynes, aldehydes, ketones and imines. Several transition metals may be used, for example Rh, Ru, Ir, Co, Ni, Pd, Pt, Fe, Cr, W and Os. The catalyst may consist of a preformed complex of the metal with the ligand. In these complexes the metals may carry other ligands, for example halogen atoms; hydride; carboxylates; CO; solvents, for example acetonitrile, ether and the like; nitrogen bases, like pyridine, quinoline and dimethylaniline; olefins for example ethene; or dienes for example cyclooctadiene; aryl groups bound through all or part of their π -orbitals for example η -6 benzene, or η -6 cumene. The complexes may be positively or negatively charged, or even carry more than a single charge. In this case the complex will have a counter anion

for example a halide ion, a tosylate, a carboxylate, a composite anion, for example BF_4^- , PF_6^- , $\text{B}(\text{C}_6\text{F}_5)_4$, in case of a cationic complex, and a counteranion, for example Na^+ , K^+ , Ca^{2+} , in case of an anionic complex. It might also
5 be advantageous to treat a complex of the transition metal and the ligand of the invention, which may contain other ligands, with bases, for example aqueous NaOH , or aqueous bicarbonate. It may also be advantageous to use as
10 catalyst a reduced form of said complex, which can be prepared by treating the complex with a reducing agent, for example NaBH_4 , LiAlH_4 , Zn powder, H_2 , alcohols, trialkylamines, and the like.

It may also be advantageous to use a catalyst precursor for example $[\text{Rh}(\text{COD})\text{Cl}]_2$ or $\text{Pd}(\text{DBA})_2$ in
15 conjunction with the ligand of the invention.

The ratio between catalyst and substrate in general varies in between 10^{-1} and 10^{-6} , but will usually lie between $2 \cdot 10^{-2}$ and $5 \cdot 10^{-5}$.

The hydrogenation is carried out with hydrogen
20 at pressures between 0.01 and 100 MPa, but more usually will be carried out at pressures between 0.1 and 10 MPa. The hydrogenation can also take the form of a transfer hydrogenation. In this case no hydrogen gas is used but hydrogen is transferred from a reducing agent, for example
25 secondary alcohols, like isopropanol; aromatic alcohols like benzyl alcohol; formic acid or salts thereof; or hypophosphorous acid or salts thereof.

The hydrogenation can be performed in a solvent or carried out in the absence of solvent; in this case the
30 starting material and/or the product will be the solvent.

The ligands of the invention can also conveniently be used in conjunction with a variety of transition metals as catalysts for the isomerisation of olefins, dienes, polyenes, alkynes; allyl ethers are
35 converted to enol ethers, allyl amines to enamines, allyl amides to enamides, allyl alcohols to ketones, and epoxides to aldehydes and/or ketones. Isomerisation

processes in a general sense have been described extensively in Penny Chaloner, "Handbook of Coordination Catalysis in Organic Chemistry". From this article it becomes clear what the expected products of these isomeri-
5 sation reactions are and what the scope is of these isomerisation reactions. The ligands of the invention can be advantageously used because they form stable complexes which give high turnover numbers in these reactions. Turnover number here and hereinafter are to be understood
10 as being the number of substrate molecules that can be converted per molecule of transition metal compound.

Suitable transition metals are V, Nb, Ta, Cr, Mo, W, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, and Cu. The catalysts may take the form of a complex between the
15 transition metal and the ligand like described above for the hydrogenation catalysts, or may be prepared in situ from a suitable catalyst precursor and the ligand. It may be advantageous to add an acid like acetic acid, p-toluenesulfonic acid, trifluoroacetic acid, HCl, silica ,
20 aluminum oxide (neutral or acidic), or an acidic ion exchange resin, and the like to the reaction mixture to enhance or even enable the isomerisation activity. It might also be advantageous to treat a complex of the transition metal and the catalyst, which may contain other
25 ligands, with bases, for example aqueous NaOH, or aqueous bicarbonate and use the resulting compound as catalyst. It may also be advantageous to use as catalyst a reduced form of said complex, which can be prepared by treating the complex with a reducing agent for example NaBH₄, LiAlH₄, Zn
30 powder, H₂, alcohols, trialkyl-amines, and the like.

The ligands of the invention can also be used conveniently in transition metal catalysed cross coupling reactions. In these reactions a compound possessing a leaving group on an sp₂-carbon atom, for example aryl
35 halides, aryl triflates, aryl sulfonates, vinyl halides, vinyl triflates and vinyl sulfonates is coupled with a nucleophile for example a Grignard reagent, an

alkyllithium compound, an alkylated zinc compound, an alkyl aluminum compound, an alkyl- or aryl boronic acid or ester thereof, and other C-nucleophiles for example cyanide anion.

5 Suitable transition metals are Fe, Co, Ni, Pd and Cu. Of these Ni and Pd are preferred metals. Nickel is especially preferred.

 The actual catalyst can be a preformed complex between the transition metal and the ligand of the
10 invention as described above or may be prepared in situ from a catalyst precursor. Reaction between PdCl_2 and a ligand of the invention in a 1:1 ratio will give the complex $\text{PdCl}_2(\text{Ligand})$. Likewise NiCl_2 gives $\text{NiCl}_2(\text{Ligand})$.

 The catalyst/substrate ratio in general varies
15 between 10^{-1} and 10^{-5} , but more preferred is a ratio between 10^{-2} and $5 \cdot 10^{-4}$.

 The solvent used is dependant on the type of nucleophile. Ether type solvents are best used in
20 conjunction with Grignards and alkyllithium compounds, but other nucleophiles can tolerate a wider range of solvents.

 The preferred temperature is also dependant upon the type of nucleophile. Grignards and alkyllithium compounds can be used at temperatures between -30 and 50°C , but other nucleophiles are more tolerant of higher
25 temperatures.

 The invention will be elucidated with reference to the following non-limiting examples.

Example I

30 Preparation of 4a-10a-dihydro-2,8-dimethyl-4,6-bis(diphenylphosphine) phenoxathiine (Ligand 1; formula sheet)

 30.3 ml of s-BuLi (1.3 M in 98/2 (vol/vol) cyclohexane/hexane, 39.4 mmol), was added dropwise, at
35 -60°C , to a stirred solution of 3.0 g of dimethylphenoxathiine (13.1 mmol), 4.6 ml of TMEDE (N,N,N',N'-tetramethyl-1,2-diaminoethane) (39.4 mmol) and

250 ml of dry diethyl ether.

After all the s-BuLi had been added, the cooling bath was removed to enable the solution to reach room temperature. After 16 hours the mixture was then cooled to -60°C, after which a solution of 8.7 ml (48.5 mmol) of chlorodiphenylphosphine in 40 ml of hexane was added dropwise. The cooling bath was again removed and the reaction mixture was stirred for 16 hours. The ether was removed at reduced pressure (vacuum) and the remaining oil was dissolved in CH₂Cl₂, then washed with water, dried under N₂ with the aid of MgSO₄ and the solvent was removed in a vacuum. The residue thus obtained was washed with hexane and crystallised from 1-propanol. The white crystals obtained proved to be stable in the presence of air. The yield was 71%. The crystals were analysed. The NMR spectra were recorded with the aid of a Bruker AMX-300 FT-NMR, the IR spectra with the aid of a Nicolet 510 FT-IR. The results were:

¹H-NMR (300 MHz, CDCl₃) δ: 7.16-7.35 (Ar, 20 H) P(C₆H₅), 6.87("d", J=1.6Hz, C(P(Ph)₂)-CH-C(CH₃)), 6.23(bs, 2H, C(S)-CH-C(CH₃)), 2.07(s, 6H, CH₃).

³¹P-NMR (121.5MHz, CDCl₃) δ: -17.34.

IR: (CHCl₃, cm⁻¹): 3004(m), 2961(m), 2926(m), 1435(s), 1407(vs), 1244(m), 695(m).

Example II

Preparation of 4a,9a-dihydro-9,9-dimethyl-4,5-bis(diphenylphosphino) xanthene (Ligand 2; formula sheet)

11 ml of s-BuLi (1.3M in 98/2 (vol/vol) cyclohexane/hexane, 14.3 mmol) was added dropwise, at room temperature, to a stirred solution of 1.0 g of 9,9-dimethylxanthene (4.8 mmol) and 2.3 ml of TMEDE (14.3 mmol) and 50 ml of dry diethyl ether. The reaction mixture was stirred for 16 hours.

Then the mixture was cooled to 0°C and a solution of 2.6 ml of chlorodiphenylphosphine (14.3 mol) in 5 ml of tetrahydrofuran was added dropwise. A

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suspension was formed. This mixture was stirred for 4 hours. The solvent was removed at reduced pressure and the resulting oil was dissolved in 40 ml of CH_2Cl_2 , then washed with 15 ml of water, dried with the aid of MgSO_4 . After that the solvent was removed under a vacuum. The resultant sticky mass was washed with hexane and crystallised from 1-propanol, after which a powder was obtained. The yield was 2.05 g of yellowish white powder (yield 75%). The product proved to be stable in the presence of air in powdered form and also in a CDCl_3 solution.

As in Example I, the powder was analysed.
 $^1\text{H-NMR}$ (300MHz, CDCl_3) δ : 7.40 (dd, 2H, $J=7.8, 1.0\text{Hz}$, CP-CH-CH), 7.15-7.26 (ar, 20H) $\text{P}(\text{C}_6\text{H}_6)$, 6.96 (t, 2H, $J=7.7\text{Hz}$, CH-CH-CH), 6.54 (dd, 2H, $J=7.4, 1.4\text{Hz}$, CH-CH-CC), 1.65 (s, 6H, CH_3).
 $^{31}\text{P-NMR}$ (121.5MHz, CDCl_3) δ : -17.52.
IR: (CHCl_3 , cm^{-1}): 3073(w), 2974(w), 1435(s), 1405(vs), 1243(m), 695(m).

Example III

20 Hydroformylation of 1-octene with ligand 1 and Rh

A 180-ml stainless steel autoclave with a glass liner was filled with 5 ml of a mixture of 5 mmol $\text{Rh}(\text{acac})(\text{CO})_2$ and toluene ($25 \cdot 10^{-3}$ mmol), 0.0164 g of the ligand of Example I ($27.5 \cdot 10^{-3}$ mmol), and 3.0 ml of 1-octene. The total volume was 8.6 ml, the Rh/substrate ratio was $1.5 \cdot 10^{-3}$. The pressure at the beginning of the reaction was 1.0 MPa (1:1 (mol:mol) $\text{CO}:\text{H}_2$) and the temperature was 40°C . The reaction was carried out batchwise. No additional carbon monoxide or hydrogen was added during the reaction. The results are shown in Table 1.

Examples IV-VI

Hydroformylation of 1-octene with ligand 1 and Rh

35 Example III was repeated using a variable ligand/rhodium (L/Rh) ratio as indicated in Table 1. The results are shown in Table 1.

Example VIIHydroformylation of 1-octene with ligand 1 and Rh

Example III was repeated at 80°C. The results are shown in Table 1.

5

Comparative Experiment AHydroformylation of 1-octene with BISBI and Rh

Example VII was repeated using 2,2'-bis(diphenylphosphinomethyl)-1,1'-biphenyl (BISBI), as the ligand. The results are shown in Table 1.

10

Comparative Experiment BHydroformylation of 1-octene with BISBI and Rh

Example III was repeated using BISBI as the ligand. The results are shown in Table 1.

15

Example VIIIHydroformylation of 1-octene with ligand 1 and Rh

Example III was repeated at 100°C. The results are shown in Table 1. From the results it can be seen that at a higher temperature the degree of conversion is higher, but the selectivity towards the aldehyde is lower.

20

T A B L E 1

Example/ Experi- ment	L/Rh	time (hr)	degree of conversion (%) (1)	isomerisation sel. (%) (2)	sel. aldehyde (%) (3)	n/iso (4)	sel. n- aldehyde (%) (5)
5	III	1.1	5.17	12.5	9.6	90.4	5.7
	IV	2.2	22.10	31.8	6.4	93.6	44.9
	V	5.0	16.0	30.3	6.7	93.3	45.1
	VI	10.0	19.5	34.1	5.1	94.9	45.4
	VII	2.2	1.05	67.4	7.2	92.8	53.0
		10.0	98.7	4.7	95.3	41.4	93.1
10	VIII	2.2	0.08	38.4	15.5	84.5	33.7
		0.17	55.9	14.5	85.5	44.9	83.6
		0.25	72.5	14.8	85.2	38.0	83.0
15	A	2.2	0.17	49.8	20.8	79.2	15.8
		1.25	98.3	10.7	89.3	4.1	71.8
	B	1.1	2.0	53.1	94.9	5.1	4.0

(1) molar percentage of converted 1-octene

(2) molar selectivity towards internally unsaturated octene (isomerisation to 2-octene)

(3) molar selectivity towards total aldehyde (= normal + iso aldehyde)

(4) n/iso molar ratio

(5) molar selectivity towards n-aldehyde

Example IXHydroformylation of 1-octene with ligand 2 and Rh

Example III was repeated using the ligand of Example II at 40°C. The results are shown in Table 2.

5

T A B L E 2

10	L/Rh	time (hr)	degree of conversion (%)(1)	isomeri- sation (%)(2)	sel. aldehyde (%)(3)	n/iso (4)	sel. n- aldehyde (%)(5)
	2.2	0.08	18.8	4.0	96.0	49.9	94.1
		0.17	22.9	4.3	95.7	44.6	93.6
15		0.25	34.9	7.3	92.7	50.9	90.9
		0.45	74.2	7.2	92.8	49.4	91.0

(1)-(5) see legend Table 1.

20 For all the given results the selectivity towards the total amount of aldehydes is 100% minus the percentage of the 1-octene that has isomerised to internally unsaturated octenes (see Tables 1 and 2). These internally unsaturated octenes are undesired by-products when terminal aldehydes
25 are being prepared, because these octenes are generally not very reactive and, if they do react, they are converted with a high selectivity into the undesired iso aldehyde.

When the results of Example VII and Comparative Experiment
30 A (or Example III and Experiment B) are compared it can be seen that a higher selectivity and yield of total aldehydes and a higher n/i ratio are obtained when use is made of the bidentate phosphine ligand according to the invention than when use is made of the bidentate phosphine
35 ligand according to WO-A-8707600.

Example XHydroformylation of styrene with ligand 2 and Rh

Example III was repeated using the ligand of Example II in a L/Rh ratio of 2.2 and styrene as
 5 substrate. The Rh/substrate ratio was $1.5 \cdot 10^{-3}$. The amount of Rh used was 1.78 mmol. The results are shown in Table 3.

Comparative Experiment C10 Hydroformylation of styrene with PPh_3 and DIOP and Rh

Using either PPh_3 or DIOP (2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane) as ligands. The results are shown in Table 3.

15 TABLE 3

20	Ligand	T(°C)	pressure (MPa)	n/iso	% n-aldehyde	TOF (hr ⁻¹) ^b
	2	60	1	0.77	44	128
	2	80	1	0.88	47	724
	2	120	1	2.35	70	4285
	PPh_3	70	6.2	0.08	7	not determined
	DIOP	25	0.1	0.25-0.49 ^a	20-33 ^a	not determined

^a Depending upon rhodium precursor used

25 ^b Turnover frequency in mol converted substrate per mol transition metal compound per hour.

Example XIPreparation of 4,6-bis(diphenylphosphino)-
10,10dimethylphenoxasilin

At room temperature a solution of 8.00 g of
5 diphenylether (47.0 mmol) in 35 ml of THF was added
dropwise to a mixture of 41.4 ml of 2.5 M n-butyllithium
in hexane (103.4 mmol) and 16.7 ml of TMEDA (103.4 mmol).
When all phenylether was added, the reaction mixture was
stirred for 16 h. The ethereal solution of 2,2'-
10 dilithiodiphenylether and a solution of 5.7 ml of
dimethyldichlorosilane (47.0 mmol) in 75 ml of ether were
added simultaneously to 40 ml of ether over 1 h. The
reaction mixture was stirred for 16 hr. then hydrolyzed by
addition of 30 ml of water. The hydrolyzed mixture was
15 stirred for 2 hr. The organic layer was separated, and the
aqueous layer was extracted with 30 ml of ether. The
combined organic layers were treated with Norit, and dried
with MgSO_4 . The solvent was removed in vacuo. Small
crystals formed during the concentration. The semisolid
20 oil was crystallized from methanol, resulting in white
crystals of 10,10-dimethylphenoxasilin with a grassy odour.
Yield: 4.82 g (45%).

^1H NMR (CDCl_3) δ : 7.56 (dd, 2H, $J=7.2$, 1.7Hz), 7.45
(dt, 2H, $J=7.7$, 1.7Hz), 7.22 (d, 2H, $J=8.4$ Hz), 7.17 (dt,
25 2H, $J=7.2$, 0.9Hz), 0.51 (s, 6H, $(\text{CH}_3)_2\text{Si}$); $^{13}\text{C}\{^1\text{H}\}$ NMR
(CDCl_3) δ : 160.2, 134.5, 131.7, 123.1, 119.7 (C-Si), 118.5,
0.2 ($(\text{CH}_3)_2\text{Si}$); IR: CHCl_3 , cm^{-1} : 3070, 3008 2957, 2901,
1604, 1593, 1574, 1426, 1370, 1301, 1270, 885, 845, 807;
exact mass (MS): 226.0808 (calc. $\text{C}_{14}\text{H}_{14}\text{OSi}$: 226.0814).

30 At room temperature 12.6 ml of sec-butyllithium
(1.3 M in 98/2 cyclohexane/hexane, 13.3 mmol) was added
dropwise to a stirred solution of 1.00 g of 10,10-
dimethylphenoxasilin (4.42 mmol) and 2.1 ml of TMEDA (13.3
mmol) in 50 ml dry ether. When all sec-butyllithium was
35 added the reaction mixture was stirred for 16 hours. Then
a solution of 2.6 ml of chlorodiphenylphosphine (13.3
mmol) in 15 ml of hexanes was added dropwise, and the

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reaction mixture was stirred for 16 hours. The solvent was removed in vacuo, the resulting solid oil was dissolved in CH_2Cl_2 , washed with water, dried with MgSO_4 , solvent removed in vacuo. The resulting oil was washed with hexane, and crystallized from 1-propanol. The resulting white crystals are air stable. Yield: 1.78 g white crystals (68%).

^1H NMR (CDCl_3) δ : 7.50 (dd, 2H, $J=7.2, 1.7$ Hz, CHCHCSi), 7.16-7.31 (ar, 20H, $\text{P}(\text{C}_6\text{H}_5)_2$), 7.00 (t, 2H, $J=7.3$ Hz, PCCHCHCH), 6.79 (dq, 2 H, $J=7.5, 1.7$ Hz, OCPCH), 0.50 (s, 6 H, $(\text{CH}_3)_2\text{Si}$); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) δ : -17.6; $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ : 137.9 (t, $J=6.8$ Hz); through-space P-P coupling ≥ 60 Hz, 136.4, 134.5, 133.9 (t, $J=10.6$ Hz, $\text{P}-\text{C}(\text{Ph})$), 127.9, 127.3 (t, $J=10.9$ Hz, CO), 122.8, 118.5, -0.4 ($(\text{CH}_3)_2\text{Si}$); IR: (CHCl_3 , cm^{-1}): 3059, 3007, 2960, 1580, 1572, 1434, 1399, 1370, 1120, 885, 857; exact mass (MS): 595.1741 (M+H) (calc. $\text{C}_{38}\text{H}_{32}\text{OP}_2\text{Si}$: 594.1698); mp: 245-245.5°C. Anal. Calcd. for $\text{C}_{38}\text{H}_{32}\text{OP}_2\text{Si}$: C, 76.75; H, 5.43. Found: C, 76.04; H, 5.61.

Example XII

Hydrocyanation of styrene with ligands 1, 2 and 4 and Ni

2.0 ml of a 73.3 mM solution of $\text{Ni}(\text{COD})_2$ in toluene (0.147 mmol) was added to a Schlenk-vessel containing a stirring bar and 0.176 mmol of the ligand of Example I, II or XI. This reaction mixture was stirred for 2 hours, to ensure complete formation of the catalyst.

0.336 ml of styrene was added (433 mg, 4.15 mmol), and the reaction mixture was stirred for another 30 minutes.

The reaction mixture was then cooled to ca. -40°C , 0.100 ml of liquid HCN (2.58 mmol) was added, and the Schlenk vessel was placed in a thermostated heating bath of the desired temperature.

After 19 hours, the stopper was removed to allow HCN (which was possibly still present) to evolve from the reaction mixture. After ca. 15 minutes the evolution of HCN was tested with a portable HCN-detector. When the

concentration of HCN immediately above the Schlenk was below 5 ppm (MAC-value is 10 ppm), the crude reaction mixture was centrifuged, the supernatant weighed.

The reaction mixture was analysed with temperature controlled gas chromatography, using diphenylether and ethyl benzene as standards for the mass balance. The result with various ligands is depicted in the Table 4.

TABLE 4

Ligand	Ligand/ Ni	Temp °C	time (hr)	Con- ver- sion %	Selec- tivity iso* (%)	Selec- tivity n* (%)	iso/ n
1	1.2	60	18	66	63	1.6	39.4
1	2.2	60	18	75	66	1.0	66.0
1	1.2	21	18	74	54	1.1	49.1
1	2.2	21	18	59	54	0.6	90.0
2	1.2	60	18	74	53	1.7	31.2
2	2.2	60	18	79	66	2.3	28.7
2	2.2	21	18	64	56	1.2	46.7
4	1.2	60	18	75	57	3.5	16.3
4	2.2	60	18	81	62	1.9	32.6
4	1.2	21	18	73	63	2.5	25.2
4	2.2	21	18	57	53	1.4	37.9

* n = 2-Phenyl-propionitrile; iso = 1-Phenyl-propionitrile

Comparative experiment D

Hydrocyanation of styrene with Ni

Example XIII was repeated using DPPB, DPPE and DPPP as ligands. The results are shown in Table 5.

TABLE 5

Ligand	L/Ni	T (°C)	time (hr)	Conver- sion %	Selec- tivity iso* %	Selec- tivity n* %	iso/ n %
DPPB ^a	1.2	60	18	14	35	1.5	23.3
DPPE ^b	1.2	60	18	52	0.5	0.6	0.8
DPPP ^c	1.2	60	18	39	7	0.9	7.8

- 10 ^a 1,4-Bis-diphenylphosphino-butane (DPPB)
 ^b 1,2-Bis-diphenylphosphino-ethane (DPPE)
 ^c 1,3-Bis-diphenylphosphino-propane (DPPP)
 * see Table 4.

15

Example XIVCross coupling between 2-BuMgCl and Bromobenzene with ligands 2 and 4 and Pd

20 To a suspension of 0.04 mmol (diphosphine) PdCl₂ in 10 ml of ether, 4 mmol of halide and 0.4 ml of decane (2.05 mmol, internal standard) were added, followed by 8 mmol of Grignard reagent in 10 ml of ether. The reaction vessel was kept at a constant temperature using a water bath.

25 At regular intervals ca. 1 ml of the reaction mixture was quenched in 1 ml of 10% aqueous HCl, and analysed by temperature controlled gas chromatography. The reported turn over frequencies were measured after 15 minutes.

30 The results with ligands from Experiment II and XI are given in Table 6.

TABLE 6

Ligand	Temp (°C)	Pd (10 ⁻⁵ mol)	time (hr)	Conv r- sion (%)	Sel. Cross Coupling ^a (%)	Sel. Homo Coupling ^b (%)
2	0	4.0	0.25	3	56	44
2	0	4.0	23	100	79	21
2	20	3.3	0.25	5	60	40
2	20	3.3	4	9	60	40
4	20	4.1	0.25	9	86	14
4	20	4.0	0.25	13	83	17

a: i-Bu-benzene + n-Bu-benzene

10 b: Biaryl and octanes

Example XIII

Carbonylation of butadiene with ligand 2 and Pd

15 A Parr autoclave, made of Hastelloy C, was filled successively with 0.18 mmol of palladium(II)acetate, 0.20 mmol of the ligand of Example II, 2.7 mmol of 2,4,6-trimethylbenzoic acid, and 19 g of diphenyl ether. The autoclave was closed and purged three times with 4.0 MPa carbon monoxide. Next, under a pressure of 1.0 MPa CO and

20 with stirring at a speed of 1250 rpm, a mixture of 31 mmol methanol, 0.232 g nonane (internal standard for GC product analysis), 0.231 g of cyclohexane (internal standard for butadiene GC analysis), and 29 mmol of butadiene was injected under pressure from an injection vessel into the

25 autoclave. The reaction mixture was brought to a temperature of 140°C at a CO pressure of 6.5 MPa. After 1.5 hours the reaction mixture was analyzed for the butadiene and the reaction products by gas chromatographic methods.

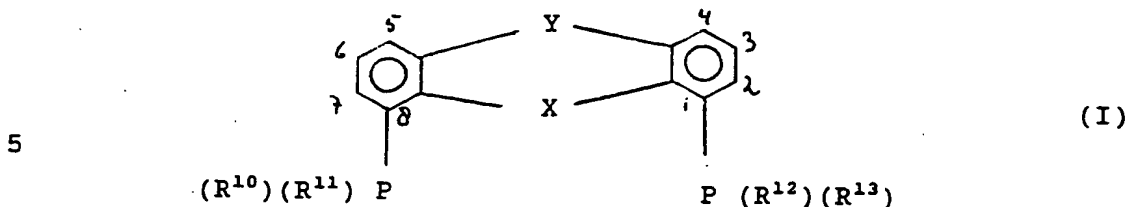
- 32 -

The conversion was: 59 %. The selectivity to methyl
pentenoates was: 92 %.

C L A I M S

1. Bidentate phosphine ligand, the phosphorus atoms of the phosphine being connected via a bridge group, characterised in that the bridge group of the bidentate phosphine ligand consists of an ortho-anellated annular system, comprising two aryl groups, which aryl groups are connected by two bridges, a first bridge consisting of an -O- or an -S- atom and a second bridge being a group that contains an oxygen, sulphur, nitrogen, silicon or carbon atom or a combination of these atoms, the phosphorus atoms being connected to the two aryl groups of the bridge group at the ortho position relative to the -O- or -S- atom of the first bridge.
2. Bidentate phosphine ligand according to Claim 1, characterised in that the second bridge in the bidentate phosphine ligand contains an -O-, -S-, -N(R¹)-, -N⁺(R²)(R³)-, -Si(R⁴)(R⁵)-, -P(O)(R⁶)-, -C(R⁷)(R⁸)- group, or a combination of a -C(R⁷)(R⁸)- group with one of the groups mentioned, R¹ being a hydrogen atom, an organic group having between 1 and 20 carbon atoms or a polymer, R² and R³ being organic groups, which may or may not be the same, having between 1 and 20 carbon atoms or a polymer, R⁴ and R⁵ being organic groups, which may or may not be the same, having between 1 and 10 carbon atoms, R⁶ being a hydroxide group or an organic group having between 1 and 10 carbon atoms and R⁷ and R⁸ being organic groups, which may or may not be the same, having between 1 and 10 carbon atoms.
3. Bidentate phosphine ligand according to Claim 1 or Claim 2, characterised in that the bidentate phosphine ligand is represented by the following

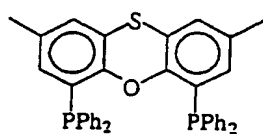
general formula (I):



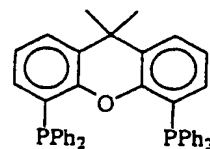
where X stands for the first bridge and Y for the second bridge and R¹⁰, R¹¹, R¹² and R¹³ stand for organic groups, which may or may not be the same, having between 1 and 14 carbon atoms.

4. Bidentate phosphine ligand according to Claim 3, characterised in that X is an -O- atom.
5. Bidentate phosphine ligand according to Claim 4, characterised in that Y does not represent an -O- atom.
6. Bidentate phosphine ligand according to any one of Claims 3-5, characterised in that R¹⁰, R¹¹, R¹² and R¹³ are aryl groups having between 6 and 14 carbon atoms, which may or may not be substituted.
7. Method for the preparation of a bidentate phosphine ligand according to any one of Claims 1-6, characterised in that an organic compound, which corresponds to the bridge group of the ligand, is dissolved in a suitable solvent, together with a strong base and an additional complexing agent, after which 2 or more equivalents of an organic phosphorus compound optionally dissolved in a solvent are added to the mixture, in which process the bidentate phosphine ligand is formed.
8. Catalyst system comprising a bidentate phosphine ligand and a transition metal compound, characterised in that the bidentate phosphine ligand is a ligand according to any one of Claims 1-6, or prepared according to claim 7.
9. Catalyst system according to Claim 8, characterised in that the molar ratio between the ligand and the

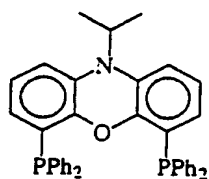
- transition metal compound is between 0.5 and 20.
10. Method for the preparation of an ald hyde, using an ethylenically unsaturated organic compound as a starting material, through hydroformylation in the presence of carbon monoxide, hydrogen and a catalyst system comprising a bidentate phosphine ligand and a transtion metal compound, characterised in that a catalyst system according to Claim 8 or Claim 9 is used.
11. Method for the preparation of an aldehyde according to Claim 9, characterized in that the transition metal compound is a rhodium compound.
12. Method for the preparation of an aldehyde according to Claim 10 or Claim 11, characterised in that the ethylenically unsaturated organic compound has between 2 and 20 carbon atoms.
13. Method for the preparation of a terminal aldehyde according to any one of Claim 10-12, characterised in that the ethylenically unsaturated compound is a terminally unsaturated organic compound.
14. Use of the bidentate phosphine ligand according to any one of Claims 1-6 as part of a catalyst system in combination with a transition metal compound, the catalyst system being used for a hydroformylation, hydrogenation, hydrocyanation, polymerisation, isomerisation, carbonylation, cross-coupling or metathesis reaction.
15. Process for the preparation of a pentenoic ester by carbonylation of butadiene in the presence of an alkanol and CO, using a catalyst system comprising a protonic acid with a $pK_a > 3$, a palladium compound and a ligand according to any one of claims 1-6.



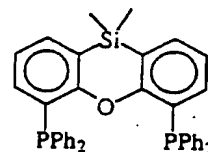
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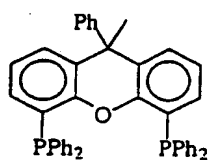
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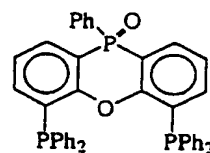
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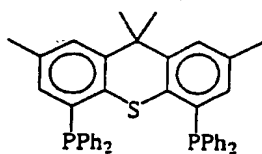
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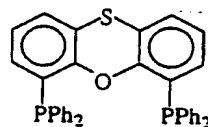
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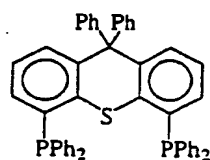
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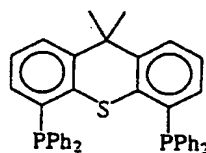
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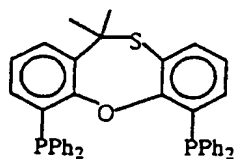
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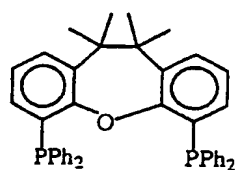
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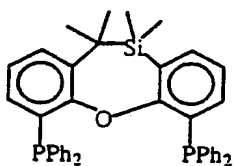
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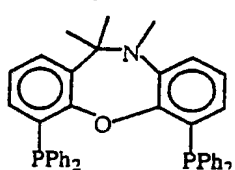
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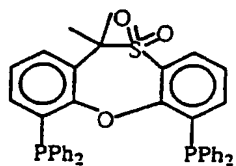
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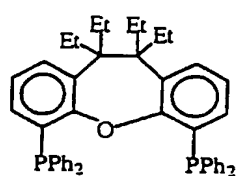
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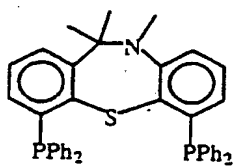
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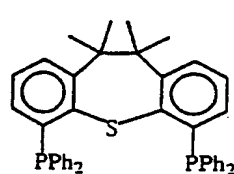
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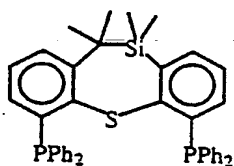
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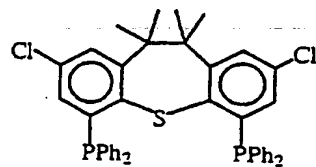
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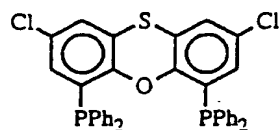
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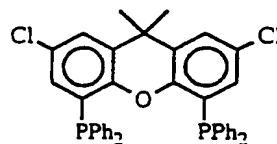
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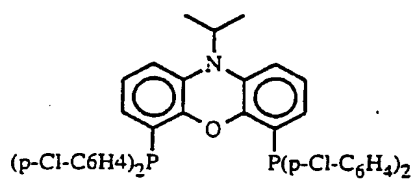
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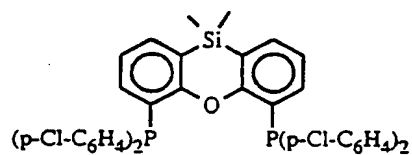
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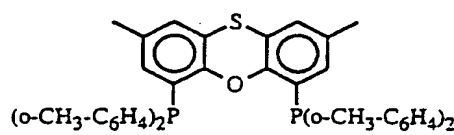
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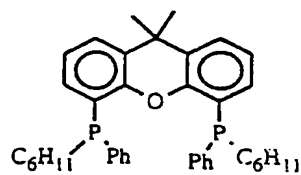
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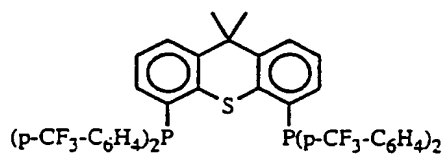
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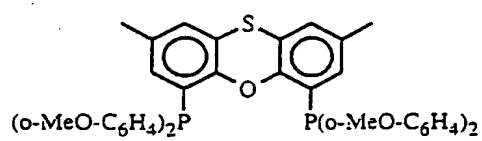
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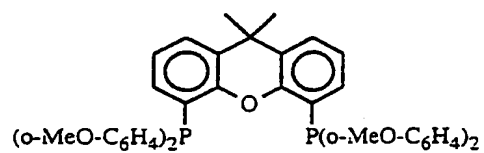
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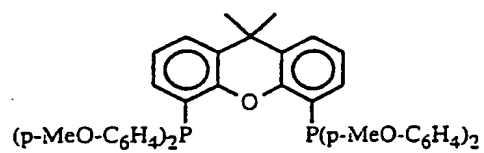
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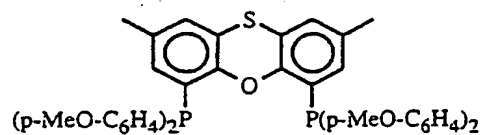
Ligand 28



Ligand 29



Ligand 30



Ligand 31

INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 95/00161

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07F9/655 C07C45/50 B01J31/24 C07F9/6536 C07F9/6571
 C07F9/6553 C07F9/6527 C07F9/6596 C07F9/6533 C07C67/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07F C07C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,87 07600 (EASTMAN KODAK CO.) 17 December 1987 cited in the application see the whole document ---	1-15
A	US,A,5 171 892 (MARK J. BURK) 15 December 1992 see the whole document ---	1-9
A	JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol.315, no.3, 1986, LAUSANNE CH pages 383 - 386 PRAMESH N. KAPOOR 'Nickel(II), Palladium(II) and Platinum(II) complexes of trans spanning ditertiary phosphine 3,3 '-oxybis((di-meta-tolylphosphino)methyl)be nzene.' see the whole document ---	1-9

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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

28 June 1995

Date of mailing of the international search report

06.07.95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax (+31-70) 340-3016

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Beslier, L

INTERNATIONAL SEARCH REPORT

Intern al Application No

PCT/NL 95/00161

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CHEMISCHE BERICHTE, vol.124, no.8, 1991, WEINHEIM DE pages 1705 - 1710 MATTHIAS W. HAENEL 'Bidentate phosphines of heteroarenes: 4,6-bis(diphenylphosphino)dibenzofuran and 4,6-bis(diphenylphosphino)dibenzothiophene see the whole document ---	1-7
A	TETRAHEDRON LETTERS, vol.34, no.13, 1993, OXFORD GB pages 2107 - 2110 MATTHIAS W. HAENEL 'Bidentate phosphines of heteroatoms: 1,9-bis(diphenylphosphino) dibenzothiophene and 4,6-bis(diphenylphos phino)dibenzothiophene.' see the whole document ---	1-7
P,X	TETRAHEDRON LETT. (TELEAY,00404039);95; VOL.36 (1); PP.75-8, MAX-PLANCK-INST. KOHLENFORSCH.;MUELHEIM AN DER RUHR; D-45470; GERMANY (DE) Hillebrand S et al 'Phosphine ligands. 4. Bidentate phosphines of heteroarenes: 9,9- dimethyl-4,5-bis(diphenylphosphino)xanthen e' see the whole document -----	1-7

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 95/00161

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-8707600	17-12-87	US-A- 4760194	26-07-88
		US-A- 4755624	05-07-88
		US-A- 4694109	15-09-87
		CA-A- 1300164	05-05-92
		EP-A, B 0279018	24-08-88
		EP-A, B 0311619	19-04-89
		JP-T- 1503533	30-11-89
		US-A- 4851581	25-07-89
		US-A- 4904808	27-02-90
US-A-5171892	15-12-92	EP-A- 0592552	20-04-94
		JP-T- 6508848	06-10-94
		WO-A- 9301199	21-01-93
		US-A- 5386061	31-01-95
		US-A- 5329015	12-07-94

(19)



Europäisches Patentamt
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(11) Publication number:

0 155 508
A1

(12)

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(22) Date of filing: 15.02.85

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C 07 F 9/65

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28.12.84 US 685025

(43) Date of publication of application:
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(71) Applicant: UNION CARBIDE CORPORATION
Old Ridgebury Road
Danbury Connecticut 06817(US)

(72) Inventor: Billig, Ernst
1575 Smith Road
Charleston West Virginia 25314(US)

(72) Inventor: Abatjoglou, Anthony George
1504 Lyndale Drive
Charleston West Virginia 25314(US)

(72) Inventor: Bryant, David Robert
1201 Shady Way
South Charleston West Virginia 25309(US)

(72) Inventor: Murray, Rex Eugene
5291 Dalewood Drive, No. 522
Charleston West Virginia 25313(US)

(72) Inventor: Maher, John Michael
1113 Highland Road
Charleston West Virginia 25302(US)

(74) Representative: Schmied-Kowarzik, Volker, Dr. et al,
Patentanwälte Dr. V. Schmied-Kowarzik Dipl.-Ing. G.
Dannenberg Dr. P. Weinhold Dr. D. Gudel Dipl.-Ing. S.
Schubert Dr. P. Barz Siegfriedstrasse 8
D-8000 München 40(DE)

(54) Transition metal complex catalyzed reactions.

(57) Transition metal-diorganophosphite complex catalyzed carbonylation processes, especially hydroformylation, as well as transition metal-diorganophosphite ligand complex compositions, diorganophosphite ligands and transition metal-diorganophosphite catalysts.

EP 0 155 508 A1